

## The Improved Synthesis and Crystal Structure of 20-Thiocrown-4

ROBIN D. ROGERS\* and RODGER F. HENRY

Department of Chemistry, Northern Illinois University, DeKalb, IL 60115, U.S.A.

LEO A. OCHRYMOWYCZ\* and STEVEN G. TOSKE

Chemistry Department, University of Wisconsin-Eau Claire, Eau Claire, WI 54702-4004, U.S.A.

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**Abstract.** An improved synthesis of 20-thiocrown-4 is reported, which exploits the Kellogg method of cesium carbonate in DMF mediated macrocyclization of precondensed synthones which converge at the cycloicosane structure. The crystal structure of 20-thiocrown-4 reveals a rectangular conformation for the free ligand. Each sulfur is in one *gauche* and one *anti* torsion angle. Four carbon positions make up the corners. There are two short sides comprised of —C—C— torsion angle sequences  $g^-ag^-$  and two long sides ( $aaa, g^-ag^+$ ). The S—C and C—C bond distances average 1.816(2) Å and 1.523(3) Å, respectively.

**Key words.** 20-thiocrown-4, X-ray crystal structure, crown ether.

**Supplementary data** relating to this article are deposited with the British Library as Supplementary Publication No. SUP 82147 (9 pages).

### 1. Introduction

Thiocrown ethers have recently generated much interest as ligands which impart unique properties to complexes of post-transitional elements [1]. Unlike the oxacrown ethers, which are almost uniformly preconformed for endodentate coordination, the thiocrown ethers containing dimethylene linkages, with the exception of 9-thiocrown-3, preconform in exodentate fashion due to a strong preference for *gauche* C—S—C—C torsion angles [1–7]. This trend is less in evidence when trimethylene linkages are utilized [8]. Systematic studies of even larger polymethylene linkage thiocrown ethers are lacking, in part, due to perceived difficulty in preparation of pure samples. However, the fortuitous observation by Kellogg [9] that cesium carbonate in DMF affords superior macrocyclization of  $\alpha,\omega$ -dihaloalkanes with  $\alpha,\omega$ -dithiolalkanes essentially free of intrachain cyclization side reactions, led us to demonstrate the general and convenient utility of this method for thiocrown ether synthesis, including 20-thiocrown-4. The crystal structure of 20-thiocrown-4 now allows the first glimpse of conformational preferences in thiocrown ethers with tetramethylene linkages.

\* Authors for correspondence.

## 2. Experimental

NMR spectra were obtained on a Bruker NR/80 FT-NMR spectrometer. Infrared spectra were obtained on a Nicolet 5DXC FT-IR spectrometer. Mass spectra were obtained on a Hewlett-Packard system 5890A series II G.C. using a HP-1 column over a 50–200°C ramp, coupled to a 5971A Mass Selective Detector. Baker Analyzed Reagent silica gel (60–200 mesh) was utilized for column chromatography and TLC analyses were performed on Whatman MKGF, 60A, 1 × 3 in. 250 μm layer plates with solvent reported as volume ratios. All reagents were Aldrich Chemical Company reagent grade materials.

### 2.1. SYNTHESIS OF 1,6,11,16-TETRATHIOCYCLOICOSANE (20-THIOCROWN-4)

#### 2.1.1. 5,10-Dithiotetradecane-1,14-diol

A mantle heated 2 L three-necked flask was equipped with a magnetic stirrer, addition funnel, condenser and continuous nitrogen purge. The flask was charged with 1 L of absolute ethanol and an ethoxide solution was generated by the slow addition of small pieces of sodium metal (10.12 g, 0.44 mol). To the ethoxide solution was added all at once (25 g, 0.204 mol) 1,4-butanedithiol and the reaction brought to reflux. The 4-chloro-1-butanol (44.17 g, 0.408 mol) was added dropwise and the mixture allowed to reflux an additional 4 h. The cooled mixture, (~5°C), was filtered to remove salt and rotary vacuum concentrated. The residue was taken up in 500 mL methylene chloride and cooled overnight at ~20°C to precipitate remaining salt, which was removed by refiltration and the solution reconcentrated by rotary vacuum evaporation. The residue was subjected to further evaporation by Kugelrohr below 80°/0.05 Torr for 1 h to yield 53.9 g (99.3%) colorless oil. TLC analysis in 80:20 chloroform/methanol,  $R_f = 0.56$ , showed a single pure component.

#### 2.1.2. 1,14-Dichloro-5,10-dithiotetradecane

To a mantle heated 1 L three necked flask equipped with a magnetic stirrer, addition funnel, condenser, and continuous nitrogen purge was added the (53.9 g, 0.203 mol) 5,10-dithiotetradecane-1,14-diol dissolved in 500 mL dry methylene chloride. Thionyl chloride (59.5 g, 0.50 mol) dissolved in 100 mL dry methylene chloride was added dropwise over 2 h. The reaction was then gently refluxed for 4 h, and 20 mL methanol was added to quench excess thionyl chloride. After 1 h, 1.5 g charcoal was added and the warm solution filtered and rotary vacuum concentrated to yield a pale yellow oil, 59.6 g (98.6%). TLC analysis in cyclohexane showed a single component,  $R_f = 0.34$ . **Caution:** Although we encountered no vesicant reaction, some halosulfides are potent vesicants and warrant extreme caution in handling.

#### 2.1.3. 1,6,11,16-Tetrathiocycloicosane (20-Thiocrown-4)

A mantle heated 5 L, greased, three-necked flask was equipped with a mechanical stirrer, two Claisen Y-extension joints fitted in order with a continuous nitrogen

purge, immersion thermometer, 500 mL addition funnel, and condenser. The flask was charged with 2.5 L dry DMF and powdered cesium carbonate (130.4 g, 0.40 mol). The stirred suspension was heated to and maintained at 80°C while a solution of 1,14-dichloro-5,10-dithiotetradecane (59.6 g, 0.197 mol) and 1,4-butanedithiol (24.13 g, 0.197 mol) in 250 mL DMF was added dropwise over 6 h. The reaction was allowed to stir for an additional 12 h, cooled, filtered, and DMF removed by rotary vacuum evaporation at 90°C. The cream-colored paste residue was taken up in 1 L of methylene chloride, washed with three 600 mL portions of 1M HCl, then 1 L water, dried with MgSO<sub>4</sub>, filtered, and reconcentrated by rotary vacuum evaporation to yield 68.5 g of colorless oil residue. The residue was dissolved in 200 mL of hot cyclohexane and the solution eluted through a 8 × 50 cm silica gel column with a 50:50 mixture of hexane–cyclohexane. The desired component was completely recovered in the initial 5 L of eluant as an oil, 20.66 g (29.7%). Crystallization from 200 mL pentane yielded 18.55 g of colorless crystals, mp = 31–32°C. TLC analysis in 75:25 hexane/pentane showed a single pure component,  $R_f = 0.40$ . IR (neat, KBr),  $\nu_{\max}$  2932, 2855, 1447, 1401, 1256, 1277, 1236, 1125, 1052, 976, 871, 752, 735, 654; <sup>1</sup>H NMR (CDCl<sub>3</sub>),  $\delta$  2.56(*dxt*, 4H,  $J \approx 3.3$  Hz), 1.72(*p*, 4H,  $J \approx 3.3$  Hz); <sup>13</sup>C NMR (CDCl<sub>3</sub>),  $\delta$  31.40(*t*), 28.35(*t*); MS,  $m/z$  352 (M<sup>+</sup>, 41), 175(19), 143(21), 87(100), 60(56), 55(56).

## 2.2. X-RAY DATA COLLECTION, STRUCTURE DETERMINATION, AND REFINEMENT FOR 20-THIOCROWN-4

A transparent single crystal of the title compound was mounted on a pin and transferred to the goniometer. The crystal was cooled to –150°C during data collection using a stream of cold nitrogen gas. The space group was determined to be either the centric  $P\bar{1}$  or acentric  $P1$ . Statistical tests indicated that the space group was centric and the subsequent solution and successful refinement of the structure was carried out in the centric space group  $P\bar{1}$ . A summary of data collection parameters is given in Table I.

The hydrogen atoms were located from a difference Fourier map and isotropically refined. Least-squares refinement with isotropic thermal parameters for all atoms led to  $R = 0.056$ . Refinement of nonhydrogen atoms with anisotropic temperature factors led to the final values of  $R = 0.024$  and  $R_w = 0.038$ . The final values of the positional parameters are given in Table II.

## 3. Results and Discussion

The original literature preparation of 20-thiocrown-4 involved the bulk condensation of 1,4-dibromobutane with sodium 1,4-butanedithiolate in 50:50 ethanol/*n*-butanol [10]. The procedure afforded the desired product in only 3.9% yield after tedious chromatographic separation from oligomeric by-products. The present sample of 20-thiocrown-4 was prepared by an adaptation of the modern generalized procedure for crown thioether synthesis [11], which involves slow addition of 1,14-dichloro-5,10-dithiotetradecane and 1,4-butanedithiol as an equimolar DMF solution to a suspension of powdered cesium carbonate in a large diluting pool of heated DMF. The resulting cyclocondensation affords 20-thiocrown-4 in superior

Table I. Data collection parameters for 20-thiocrown-4

Cmpd	20-thiocrown-4
Color/Shape	Colorless/block
For. wt.	352.69
Space group	$P\bar{1}$
Temp., °C	-150
Cell Constants <sup>a</sup>	
<i>a</i> , Å	6.237(2)
<i>b</i> , Å	11.243(1)
<i>c</i> , Å	14.112(3)
α, deg	106.12(2)
β, deg	92.74(2)
γ, deg	95.17(1)
Cell vol, Å <sup>3</sup>	944.0
Formula units/unit cell	2
<i>D</i> <sub>calc</sub> , g cm <sup>-3</sup>	1.24
<i>μ</i> <sub>calc</sub> , cm <sup>-1</sup>	4.77
Diffractometer/scan	Enraf-Nonius CAD-4/ω - 2θ
Radiation, graphite monochromator	MoK <sub>α</sub> (λ = 0.71073)
Max crystal dimensions, mm	0.38 × 0.58 × 0.58
Scan width	0.80 + 0.35 tan θ
Standard reflections	700; 0, 12, 0; 0, 0, 11
Decay of standards	± 2.5%
Reflections measured	3319
2θ range, deg	2 ≤ 2θ ≤ 50
Range of <i>h</i> , <i>k</i> , <i>l</i>	+7, ±13, ±16
Reflections observed [ <i>F</i> <sub>o</sub> ≥ 5σ( <i>F</i> <sub>o</sub> )] <sup>b</sup>	3047
Computer programs <sup>c</sup>	SHELX [13]
Structure solution	SHELXS [14]
No. of parameters varied	309
Weights	[σ( <i>F</i> <sub>o</sub> ) <sup>2</sup> + 0.00058 <i>F</i> <sub>o</sub> <sup>2</sup> ] <sup>-1</sup>
GOF	1.13
$R = \Sigma   F_o  -  F_c   / \Sigma  F_o $	0.024
<i>R</i> <sub>w</sub>	0.038
Largest feature final diff. map	0.2 e <sup>-</sup> Å <sup>-3</sup>

<sup>a</sup>Least-squares refinement of ((sin θ)/λ)<sup>2</sup> values for 25 reflections θ > 20°.

<sup>b</sup>Corrections: Lorentz-polarization.

<sup>c</sup>Neutral scattering factors and anomalous dispersion corrections from Ref. [15].

yield as the first and completely resolvable constituent eluted by column chromatography from the total condensate mixture.

Preparation of the essential intermediates proceeds in essentially quantitative yields and involves condensation of 4-chloro-1-butanol with disodium 1,4-butanedithiolate in ethanol to form 5,10-dithiotetradecane-1,14-diol and its subsequent conversion to 1,4-dichloro-5,10-dithiotetradecane. Spectroscopic data of the crude intermediates were consistent with their proposed structures. No attempt was made to purify intermediates to analytical standards in order to avoid their interim decomposition.

An ORTEP diagram of the title compound is depicted in Figure 1. Bond distances and angles are given in Table III and torsion angles can be found in Table IV. In thiocrown ethers with dimethylene linkages, there is a strong preference for

Table II. Final fractional coordinates for 20-thiocrown-4

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B</i> (eq.) <sup>a</sup>
S(1)	0.00556(5)	0.05668(3)	0.15517(3)	1.27
S(2)	-0.74579(5)	0.41899(3)	0.05420(2)	1.20
S(3)	-0.73874(6)	0.50784(3)	0.41742(2)	1.29
S(4)	-0.54442(5)	-0.01103(3)	0.34754(3)	1.35
C(1)	-0.2498(2)	0.0811(1)	0.0999(1)	1.27
C(2)	-0.2650(2)	0.2199(1)	0.1218(1)	1.18
C(3)	-0.4743(2)	0.2487(1)	0.0768(1)	1.18
C(4)	-0.5016(2)	0.3870(1)	0.1130(1)	1.26
C(5)	-0.7442(2)	0.5849(1)	0.1120(1)	1.29
C(6)	-0.7581(2)	0.6222(1)	0.2237(1)	1.21
C(7)	-0.9560(2)	0.5626(1)	0.2581(1)	1.30
C(8)	-0.9462(2)	0.5844(1)	0.3701(1)	1.41
C(9)	-0.8718(2)	0.3497(1)	0.3807(1)	1.35
C(10)	-0.7352(2)	0.2606(1)	0.4140(1)	1.26
C(11)	-0.5331(2)	0.2382(1)	0.3581(1)	1.28
C(12)	-0.3991(2)	0.1440(1)	0.3855(1)	1.42
C(13)	-0.3345(2)	-0.1031(1)	0.3720(1)	1.34
C(14)	-0.1425(2)	-0.1039(1)	0.3089(1)	1.25
C(15)	-0.1980(2)	-0.1533(1)	0.1978(1)	1.28
C(16)	-0.0291(2)	-0.1105(1)	0.1363(1)	1.31
H(1)[C(1)]	-0.349(3)	0.043(2)	0.127(1)	2.5(4) <sup>b</sup>
H(2)[C(1)]	-0.262(3)	0.040(2)	0.026(1)	2.5(4) <sup>b</sup>
H(1)[C(2)]	-0.254(3)	0.259(2)	0.195(1)	2.4(3) <sup>b</sup>
H(2)[C(2)]	-0.141(3)	0.260(1)	0.100(1)	2.0(3) <sup>b</sup>
H(1)[C(3)]	-0.594(2)	0.201(1)	0.094(1)	1.2(3) <sup>b</sup>
H(2)[C(3)]	-0.479(2)	0.222(1)	0.007(1)	1.5(3) <sup>b</sup>
H(1)[C(4)]	-0.382(3)	0.436(2)	0.100(1)	2.4(4) <sup>b</sup>
H(2)[C(4)]	-0.511(3)	0.407(2)	0.184(1)	2.9(4) <sup>b</sup>
H(1)[C(5)]	-0.608(3)	0.626(2)	0.097(1)	3.0(4) <sup>b</sup>
H(2)[C(5)]	-0.870(3)	0.606(1)	0.080(1)	1.9(3) <sup>b</sup>
H(1)[C(6)]	-0.624(3)	0.602(1)	0.254(1)	2.0(3) <sup>b</sup>
H(2)[C(6)]	-0.752(2)	0.711(2)	0.245(1)	2.0(3) <sup>b</sup>
H(1)[C(7)]	-0.975(2)	0.473(1)	0.227(1)	1.4(3) <sup>b</sup>
H(2)[C(7)]	-1.085(2)	0.597(1)	0.237(1)	1.5(3) <sup>b</sup>
H(1)[C(8)]	-1.087(3)	0.554(2)	0.388(1)	2.5(3) <sup>b</sup>
H(2)[C(8)]	-0.909(2)	0.672(2)	0.403(1)	1.9(3) <sup>b</sup>
H(1)[C(9)]	-1.006(3)	0.356(2)	0.408(1)	2.2(3) <sup>b</sup>
H(2)[C(9)]	-0.903(2)	0.321(1)	0.309(1)	1.7(3) <sup>b</sup>
H(1)[C(10)]	-0.823(3)	0.185(2)	0.405(1)	2.0(3) <sup>b</sup>
H(2)[C(10)]	-0.693(3)	0.291(2)	0.485(1)	2.4(3) <sup>b</sup>
H(1)[C(11)]	-0.580(2)	0.209(1)	0.286(1)	2.0(3) <sup>b</sup>
H(2)[C(11)]	-0.445(2)	0.312(2)	0.371(1)	1.5(3) <sup>b</sup>
H(1)[C(12)]	-0.262(3)	0.139(2)	0.355(1)	2.0(3) <sup>b</sup>
H(2)[C(12)]	-0.365(3)	0.162(1)	0.454(1)	2.0(3) <sup>b</sup>
H(1)[C(13)]	-0.405(2)	-0.185(2)	0.359(1)	1.8(3) <sup>b</sup>
H(2)[C(13)]	-0.278(2)	-0.075(1)	0.442(1)	1.8(3) <sup>b</sup>
H(1)[C(14)]	-0.074(2)	-0.022(2)	0.324(1)	1.8(3) <sup>b</sup>
H(2)[C(14)]	-0.041(2)	-0.152(1)	0.331(1)	1.5(3) <sup>b</sup>
H(1)[C(15)]	-0.332(2)	-0.125(1)	0.182(1)	1.2(3) <sup>b</sup>
H(2)[C(15)]	-0.221(2)	-0.243(2)	0.177(1)	2.0(3) <sup>b</sup>
H(1)[C(16)]	-0.066(2)	-0.151(2)	0.068(1)	2.0(3) <sup>b</sup>
H(2)[C(16)]	0.120(3)	-0.130(2)	0.156(1)	2.4(3) <sup>b</sup>

<sup>a</sup>*B* (eq.) = 4/3[*a*<sup>2</sup>β<sub>11</sub> + *b*<sup>2</sup>β<sub>22</sub> + *c*<sup>2</sup>β<sub>33</sub> + *ab*(cos γ)β<sub>12</sub> + *ac*(cos β)β<sub>13</sub> + *bc*(cos α)β<sub>23</sub>].<sup>b</sup>Isotropic refinement.

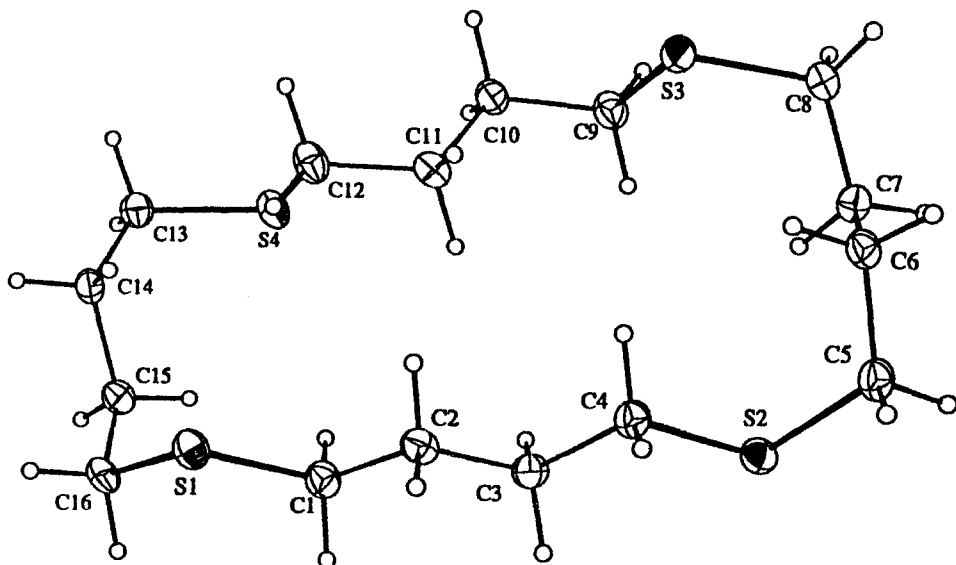


Fig. 1. ORTEP illustration of 20-thiocrown-4 with 50% probability ellipsoids. The hydrogen atoms have been given arbitrarily reduced radii.

Table III. Bond distances (Å) and angles (deg) for 20-thiocrown-4

Atoms	Distance	Atoms	Distance
S(1)—C(1)	1.816(1)	S(1)—C(16)	1.815(1)
S(2)—C(4)	1.812(1)	S(2)—C(5)	1.815(1)
S(3)—C(8)	1.816(1)	S(3)—C(9)	1.816(1)
S(4)—C(12)	1.816(1)	S(4)—C(13)	1.818(1)
C(1)—C(2)	1.517(2)	C(2)—C(3)	1.524(2)
C(3)—C(4)	1.524(2)	C(5)—C(6)	1.524(2)
C(6)—C(7)	1.516(2)	C(7)—C(8)	1.527(2)
C(9)—C(10)	1.526(2)	C(10)—C(11)	1.522(2)
C(11)—C(12)	1.525(2)	C(13)—C(14)	1.525(2)
C(14)—C(15)	1.522(2)	C(15)—C(16)	1.523(2)
Atoms	Angle	Atoms	Angle
C(1)—S(1)—C(16)	101.27(7)	C(4)—S(2)—C(5)	101.27(7)
C(8)—S(3)—C(9)	99.02(7)	C(12)—S(4)—C(13)	100.75(7)
S(1)—C(1)—C(2)	109.1(1)	C(1)—C(2)—C(3)	112.4(1)
C(2)—C(3)—C(4)	111.3(1)	S(2)—C(4)—C(3)	110.1(1)
S(2)—C(5)—C(6)	115.1(1)	C(5)—C(6)—C(7)	114.7(1)
C(6)—C(7)—C(8)	113.2(1)	S(3)—C(8)—C(7)	114.1(1)
S(3)—C(9)—C(10)	111.6(1)	C(9)—C(10)—C(11)	113.0(1)
C(10)—C(11)—C(12)	114.4(1)	S(4)—C(12)—C(11)	111.0(1)
S(4)—C(13)—C(14)	114.8(1)	C(13)—C(14)—C(15)	115.0(1)
C(14)—C(15)—C(16)	113.8(1)	S(1)—C(16)—C(15)	114.0(1)

Table IV. Torsion angles (deg) for 20-thiocrown-4

Atoms	Angle
S(1)—C(1)—C(2)—C(3)	179.3
C(1)—C(2)—C(3)—C(4)	171.1
C(2)—C(3)—C(4)—S(2)	177.6
C(3)—C(4)—S(2)—C(5)	178.2
C(4)—S(2)—C(5)—C(6)	-62.2
S(2)—C(5)—C(6)—C(7)	-58.0
C(5)—C(6)—C(7)—C(8)	170.3
C(6)—C(7)—C(8)—S(3)	-66.9
C(7)—C(8)—S(3)—C(9)	-76.7
C(8)—S(3)—C(9)—C(10)	-178.3
S(3)—C(9)—C(10)—C(11)	-69.5
C(9)—C(10)—C(11)—C(12)	-176.8
C(10)—C(11)—C(12)—S(4)	66.6
C(11)—C(12)—S(4)—C(13)	171.8
C(12)—S(4)—C(13)—C(14)	-64.5
S(4)—C(13)—C(14)—C(15)	-59.1
C(13)—C(14)—C(15)—C(16)	158.6
C(14)—C(15)—C(16)—S(1)	-63.2
C(15)—C(16)—S(1)—C(1)	-68.6
C(16)—S(1)—C(1)—C(2)	171.8

*gauche* ( $\pm 60^\circ$ ) C—S—C—C torsion angles [1–7]. Thus, every occurrence of such an angle in 18-thiocrown-6 [1, 5] and 12-thiocrown-4 [1, 5] and all but two in 15-thiocrown-5 [1, 5] is *gauche*. A consequence of this for cyclic structures is a preponderance of *anti* S—C—C—S torsion angles: all four in 12-thiocrown-4, four of five in 15-thiocrown-5, and four of six in 18-thiocrown-6. When trimethylene linkages are utilized strong torsion angle preferences are not observed [8].

20-Thiocrown-4 (with tetramethylene linkages) exhibits a rectangular conformation with one *gauche* and one *anti* C—S—C—C torsion angle at each sulfur position. The corners (two consecutive *gauche* angles of the same sign) involve C(5), C(8), C(13), and C(16). The rectangular shape is generated by the sequence of —C—C— torsion angles. The short sides (C(5)—C(8), C(13)—C(16)) are generated by a  $g^-ag^-$  sequence of —C—C— torsion angles. The long sides have the sequence *aaa* (C(1)—C(4)) and  $g^-ag^+$  (C(9)—C(12)).

Interestingly, the bond angles around each carbon seem to be influenced by conformation. The angles around carbon atoms in the short sides are larger ( $114.3(7)^\circ$  C(5)—C(8),  $114.4(5)^\circ$  C(13)—C(16)) than those angles in the longer sides ( $111(1)^\circ$  C(1)—C(4),  $113(1)^\circ$  C(9)—C(12)). This is most pronounced for the C(1)—C(4) segment containing all *anti* C—C torsion angles. All sixteen S—C—C or C—C—C angles have a  $6^\circ$  range ( $115.1(1)$  to  $109.1(1)^\circ$ ) corresponding to 60 times the standard deviation of each angle.

The more rigid macrocycle 2,2',5,5'-bis(tetramethylenedithio)-di-1,3,4-thiadiazole [12], has two —S(CH<sub>2</sub>)<sub>4</sub>S— sides. These sides exhibit the same conformation we observe for C(1)—C(4). The three —C—C— torsion angles are all *anti* and the angles around carbon average  $112(1)^\circ$ . In addition the S...S distance across the (CH<sub>2</sub>)<sub>4</sub> group is 6.917 Å, similar to the 6.827(1) Å observed for the title compound.

The bond distances observed in 20-thiocrown-4 are typical of thiocrown ethers. The S—C bonds average 1.816(2) Å with a narrow 0.006 Å range, while the C—C bonds have a 0.011 Å range and average 1.523(3) Å. These values are within the range observed for similar distances in 12-thiocrown-4, 15-thiocrown-5, 18-thiocrown-6, and 12-thiocrown-3 (S—C = 1.797(8)–1.84(1) Å, C—C = 1.440(9)–1.528(8) Å). The average C—S—C bond angle of 100.6(9)° in the title compound is also quite normal.

The four sulfur donor atoms are arranged in a flattened tetrahedron about the center of the crown ring. The S···S nonbonded contacts across the short sides of the rectangular conformation are S(1)···S(4) = 4.613(1) Å, S(2)···S(3) = 4.940(1) Å. The S(1)···S(2) contact of 6.827(1) Å (with all *anti* —C—C— torsion angles between them) is the longest in the remaining two sides with S(3)···S(4) = 5.888(1) Å. The diagonal contacts are S(1)···S(3) = 7.513(1) Å and S(2)···S(4) = 7.335(1) Å. Each sulfur atom has two intermolecular S···S contacts near 4 Å. These range from 3.740(1) to 4.247(1) Å.

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## References

1. S. R. Cooper and S. C. Rawle: *Structure and Bonding*, Vol. 72, Springer Verlag, Berlin, pp. 1–72, 1990.
2. S. G. Murray and F. R. Hartley: *Chem. Rev.* **81**, 365 (1981).
3. R. S. Glass, G. S. Wilson, and W. N. Setzer: *J. Am. Chem. Soc.* **102**, 5068 (1980).
4. J. R. Hartman, R. E. Wolf, B. M. Foxman, and S. R. Cooper: *J. Am. Chem. Soc.* **105**, 131 (1983).
5. R. E. Wolf, Jr., J. R. Hartman, J. M. E. Storey, B. M. Foxman, and S. R. Cooper: *J. Am. Chem. Soc.* **109**, 4328 (1987).
6. D. Sellmann, P. Lechner, M. Moll, and F. Knoch: *Z. Naturforsch.* **46b**, 209 (1991).
7. D. Sellmann, P. Frank, and F. Knoch: *J. Organomet. Chem.* **339**, 345 (1988).
8. S. C. Rawle, G. A. Admans, and S. R. Cooper: *J. Chem. Soc., Dalton Trans.* 93 (1988).
9. J. Buter and R. M. Kellogg: *J. Chem. Soc. Chem. Commun.* 466 (1980).
10. L. A. Ochrymowycz, C.-P. Mak, and J. D. Michna: *J. Org. Chem.* **39**, 2079 (1974).
11. R. E. Wolf, J. A. R. Hartman, L. A. Ochrymowycz, and S. R. Cooper: *Inorg. Synth.* **25**, 122 (1989).
12. S. G. Cho, F. R. Fronczek, W. S. Taylor, and S. F. Watkins: *Acta Crystallogr.* **C44**, 769 (1988).
13. G. M. Sheldrick: *SHELX76, A System of Computer Programs for X-ray Structure Determination*, as locally modified, University of Cambridge, England, 1976.
14. G. M. Sheldrick: *SHELXS, Acta Cryst.* **A46**, 467 (1990).
15. *International Tables for X-ray Crystallography*, Kynoch Press, Birmingham, England, Vol. IV, 1974, pp. 72, 99, 149. Present distributor: Kluwer Academic Publishers, Dordrecht.